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(54) Abstract Title: **Hydrophobic gypsum**

(57) A method of preparing a hydrophobic mineral and/or filler comprises contacting the mineral and/or filler in powder form with a hydrolyzable organosilane, water and a catalyst for hydrolysis and condensation of the organosilane under conditions such that the organosilane is hydrolysed in the presence of the mineral and/or filler and the organosilane hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler. The mineral and/or filler may be stucco and optionally gypsum. The organo-silane may be methyltrimethoxysilane, vinyltrimethoxysilane, methyltripropoxysilane, methyltriactoxysilane, or alkenyltriacetoxysilane. The catalyst may be a base or an alkoxide of titanium, zirconium, vanadium or aluminium, an organic compound of tin or a fluoride salt. Also disclosed is a method of forming a hydrophobic mineral and/or filler without using a catalyst and a hydrophobic gypsum having a water uptake of less than 25%.

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HYDROPHOBIC GYPSUM

[0001] This invention relates to a process of making a mineral or filler hydrophobic and/or water resistant. The invention is particularly applicable to gypsum and gypsum products.

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[0002] Gypsum products such as gypsum plasterboard are made by mixing stucco with water to produce a slurry. The slurry is fed onto a sheet of cardboard, covered with a second sheet of cardboard, and passed over a molding platform to be shaped into an encased strip. The strip of gypsum plasterboard is initially soft, but then quickly sets as the 10 calcium sulfate hemihydrate (stucco) rehydrates back to calcium sulfate dihydrate (gypsum), and therefore hardens, and is cut into separate panels of gypsum plasterboard.

[0003] In particular, gypsum plasterboard is produced from basic materials including paper in the form of cardboard, stucco, water, starch, and additives such as accelerators and 15 foams. Other additives for making gypsum plasterboard are also added, including retarders such as proteins and organic acids; viscosity modifying agents; anti-burning agents; water-resisting chemicals such as polysiloxanes and wax emulsions; glass fibers; fire-resistance enhancers such as vermiculite, clays, and fumed silica; and polymeric compounds such as 20 polyvinyl alcohol. Wallboards or plasterboards are large thin gypsum panels covered with cardboard. This invention relates to an improved process for the incorporation of polysiloxane in gypsum, a gypsum product or another mineral or filler to impart water resistance.

[0004] WO-A-81/01702 describes a process for the preparation of a plaster mortar 25 containing gypsum powder, water, conventional additives and ballast material, comprising adding said materials during the process of manufacture, in the preparation of the gypsum powder, in the mixing of the powder and water or to the mixing water or to the wet mortar, alkoxysilanes and optionally a solvent and optionally a tenside/emulsifier/surfactant and 30 optionally a silanol polymerisation catalyst and optionally substances providing for acid or basic reaction conditions in the mixing water and optionally a fine powder consisting of reactive silica.

[0005] A method according to one aspect of the invention of preparing a hydrophobic mineral or filler according to the invention comprises contacting the mineral or filler in powder 35 form with a hydrolyzable organosilane, water and a catalyst for hydrolysis and condensation

of the organosilane under conditions such that the organosilane is hydrolysed in the presence of the mineral or filler and the organosilane hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler.

- 5 [0006] The mineral or filler, hydrolyzable organosilane and water are preferably contacted with a catalyst to accelerate the hydrolysis and condensation of the organosilane. Thus a method of preparing hydrophobic gypsum according to one aspect of the invention comprises mixing stucco with a hydrolysable organosilane and contacting the resulting mixture with a catalyst for hydrolysis and condensation of the organosilane, water being  
10 present when the said mixture is contacted with the catalyst.

- 15 [0007] A method of preparing hydrophobic gypsum according to another aspect of the invention comprises mixing stucco with a hydrolysable organosilane and simultaneously with a catalyst for hydrolysis and condensation of the organosilane, water being present as the stucco, organosilane and catalyst are mixed.

- 20 [0008] The invention also includes hydrophobic gypsum, characterized in that the gypsum incorporates organopolysiloxane formed by condensation of an organosilane in the presence of the gypsum, the hydrophobic gypsum having a water uptake of below 25% by weight.  
25 [0009] The process of the invention can be used for the treatment of a wide range of minerals or fillers in powder form. One example is in the preparation of hydrophobic gypsum and gypsum products, and the invention will be described in terms of gypsum although it can be applied to other minerals and fillers. As used herein, the term gypsum is intended to mean all solid forms of calcium sulfate including calcium sulfate dihydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

- The term stucco is intended to mean calcium sulfate hemihydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , commonly known as plaster of Paris or calcined gypsum. Stucco is made by heating gypsum to remove  $3/2 \text{ H}_2\text{O}$  molecule. The method of preparing hydrophobic and/or water resistant gypsum and gypsum products according to the invention, can be used to prepare hydrophobic gypsum and gypsum products derived from all sources of gypsum and stucco, including natural gypsum (calcium sulfate dihydrate), synthetic gypsum from plasterboard waste stations, or synthetic gypsum (desulphogypsum) produced at coal fired power plants that convert sulfur dioxide to synthetic gypsum, and other forms of synthetic gypsum such as titanogypsum, fluorogypsum or phosphogypsum. The method of the invention is particularly

suitable for treating stucco in powder form, as used in the preparation of gypsum products such as gypsum plasterboard.

[0010] The method of the invention can be used in preparing other types of hydrophobic and/or water resistant materials such as minerals and fillers. Some representative examples include non-hydrated, partially hydrated, or hydrated fluorides, chlorides, bromides, iodides, chromates, carbonate hydroxides, hydroxides, phosphates, hydrogen phosphates, nitrates, oxides, and sulphates of sodium, potassium, magnesium, calcium, and barium; titanium dioxide, zinc oxide, aluminium oxide, aluminium trihydroxide, vermiculite, silica including fumed silica, fused silica, precipitated silica, quartz, sand, and silica gel; rice hull ash, ceramic and glass beads, zeolites, hydrous calcium silicate, silica-carbon black composite, functionalized carbon nanotubes, cement, fly ash, slate flour, bentonite, clay, mica, kaolin, talc, calcium carbonate, wollastonite, polymeric fillers, rubber particles, wood flour, wood fibers, cellulose and cellulose-containing products, aramid fibers, nylon fibres, cotton fibers, or glass fibers.

[0011] The hydrolysable organosilane in accordance with the present invention may comprise one or more silanes, each silane being the same or different and comprising one or more alkoxy groups and/or one or more acetoxy groups and/or one or more halide groups (typically chloride groups) and mixtures thereof. Hence, the hydrolyzable organosilane can for example be an alkoxy silane or acetoxy silane or a silane containing both alkoxy and acetoxy groups bonded to a silicon atom. The alkoxy silane can be a monoalkoxy silane, dialkoxy silane, trialkoxy silane, or tetra-alkoxy silane. The alkoxy silane can contain the same or different alkoxy groups. Optionally, it may contain one or more halogenated substituted organic groups. The alkoxy silane can be an alkylalkoxy silane, arylalkoxy silane or alkenylalkoxy silane. Mixtures of alkoxy silanes can be used, or a mixture of alkoxy silane with acetoxy silane can be used.

[0012] One group of organosilanes suitable for use in the method of the invention are trialkoxy silanes having the formula  $\text{RSi}(\text{OR}')_3$ , wherein R represents an alkyl or alkenyl group having 1 to 18 carbon atoms and R' represents an alkyl group having 1 to 4 carbon atoms. Examples of alkyl trialkoxy silanes include methyltrimethoxysilane, methyltriethoxysilane, methyltri-n-propoxysilane, methyltri-i-propoxysilane, methyltri-n-butoxysilane, methyltri-i-butoxysilane, methyltri-sec-butoxysilane, methyltri-t-butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltri-n-propoxysilane, ethyltri-i-propoxysilane, ethyltri-n-butoxysilane,

ethyltri-i-butoxysilane, ethyltri-t-butoxysilane, n-propyltrimethoxysilane, n-propyltrimethoxysilane, isopropyltrimethoxysilane, n-butyltrimethoxysilane, isobutyltrimethoxysilane, isobutyltrimethoxysilane, pentyltrimethoxysilane, pentyltrimethoxysilane, hexyltrimethoxysilane, n-octyltrimethoxysilane, n-octyltrimethoxysilane,  
5 iso-octyltrimethoxysilane, chloromethyltrimethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, chloroethyltrimethoxysilane, chloropropyltrimethoxysilane, chloropropyltrimethoxysilane, trifluoropropyltrimethoxysilane, trifluoropropyltrimethoxysilane, trifluoropropyltri-n-propoxysilane, trifluoropropyltri-i-propoxysilane, trifluoropropyltri-n-butoxysilane,  
10 trifluoropropyltri-t-butoxysilane, methyldimethoxyethoxysilane, methyldimethoxy-n-propoxysilane, methyldimethoxy-i-propoxysilane, methyldimethoxy-n-butoxysilane, methyldimethoxy-t-butoxysilane, methyldiethoxy-n-propoxysilane, methyldiethoxy-i-propoxysilane, methyldiethoxy-n-butoxysilane and methyldiethoxy-t-butoxysilane. Examples of alkenyl  
15 trialkoxysilanes include vinyltrimethoxysilane, vinyltrimethoxysilane, vinyltri-isopropoxysilane, allytrimethoxysilane, allytrimethoxysilane, hexenyltrimethoxysilane and hexenyltrimethoxysilane or mixtures thereof. We have found that mixtures containing at least two of methyltripropoxysilane and/or methyltrimethoxysilane and/or  
20 methyltriacetoxysilane and/or alkenyltrialkoxysilane and/or alkenyltriacetoxysilane are particularly effective in the process of the invention.

[0013] Some examples of dialkyldialkoxysilanes that can be used in the method of the invention include dimethyldimethoxysilane, dimethyldiethoxysilane, ethylmethyldimethoxysilane, ethylmethyldiethoxysilane, isobutylmethyldimethoxysilane, isobutylmethyldiethoxysilane and trifluoropropylmethyldimethoxysilane. Examples of trialkylalkoxysilanes that can be used in the method of the invention include trimethylmethoxysilane, tri-n-propylmethoxysilane, trimethylethoxysilane, triethylethoxysilane, tri-n-propylethoxysilane, tri-i-propylethoxysilane and tri-n-butylethoxysilane. Examples of tetra-alkoxysilanes include tetramethoxysilane, 30 tetraethoxysilane, tetra-n-propoxysilane, tetra-i-propoxysilane, tetra-n-butoxysilane and tetra-t-butoxysilane.

[0014] Some examples of arylalkoxysilanes that can be used in the method of the invention include phenyldimethylmethoxysilane, phenylethylmethoxysilane, diphenylmethylmethoxysilane, triphenylmethoxysilane, triphenylethoxysilane,  
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phenylethyldimethoxysilane, phenylethyldiethoxysilane, phenylmethyldimethoxysilane,  
phenylmethyldiethoxysilane, phenylmethoxydiethoxysilane, phenyltrimethoxysilane,  
phenyltriethoxysilane and phenylmethyltrimethoxysilane.

5 [0015] Some examples of alkenyalkoxysilanes that can be used in the method of the invention include vinyldimethylmethoxysilane, vinyldimethylethoxysilane,  
vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinylphenyldiethoxysilane,  
triallylethoxysilane, diallylmethylethoxysilane and allyldimethylethoxysilane.

10 [0016] If desired, other types of hydrolyzable organosilanes such as acetoxy silanes can be used. The acetoxy silanes can be monoacetoxy silanes, diacetoxy silanes, triacetoxy silanes, tetra-acetoxy silanes, and mixtures thereof. Some examples of suitable acetoxy silanes include phenylmethyldiacetoxy silane, vinylmethyldiacetoxy silane, methyltriacetoxy silane, ethyltriacetoxy silane, propyltriacetoxy silane, butyltriacetoxy silane, phenyltriacetoxy silane,  
15 vinyltriacetoxy silane and tetra-acetoxy silane.

[0017] Mixtures of acetoxy silanes and alkoxy silanes can be used, for example mixtures of an alkylacetoxysilane with an alkylalkoxysilane, arylalkoxysilane or alkenylalkoxysilane. We have found that when the hydrolysable silane is a mixture of an alkyltriacetoxy silane and an  
20 alkyltrialkoxysilane, particularly good results can be achieved even without the use of a catalyst. The alkyltriacetoxy silane can be any of those listed above, for example methyltriacetoxy silane or ethyltriacetoxy silane. The alkyltrialkoxysilane can be any of those listed above, for example methyltrimethoxysilane or methyltripropoxysilane.

25 [0018] Thus according to a further aspect of the invention a method of preparing a hydrophobic mineral and/or filler comprising contacting the mineral and/or filler in powder form with a hydrolyzable organosilane and water, the hydrolysable silane being a mixture of an alkyltriacetoxy silane and an alkyltrialkoxysilane, under conditions such that the organosilane is hydrolysed in the presence of the mineral and/or filler and the organosilane  
30 hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler. The alkyltriacetoxy silane and alkyltrialkoxysilane can be mixed in any proportions, for example in the range 10:90 to 90:10 by weight, particularly 25:75 to 75:25.

35 [0019] Examples of silanes containing both alkoxy and acetoxy groups are methyldiacetoxymethoxysilane, methylacetoxymethoxysilane, vinyldiacetoxymethoxysilane,

vinylacetoxymethoxysilane, methyldiacetoxymethoxysilane and  
methylacetoxymethoxysilane.

[0020] Any suitable halosilanes or mixtures thereof may be utilised. Hence, the  
5 hydrolyzable organosilane can for example be a chlorosilane or a silane containing chloro  
and one or more alkoxy and/or acetoxy groups bonded to a silicon atom. The chlorosilane  
can be a monochlorosilane, dichlorosilane, trichlorosilane, or tetra-chlorosilane. The  
halosilane can contain the same or different halide groups. The chlorosilane can be an  
alkylchlorosilane, arylchlorosilanes or alkenylchlorosilane. Mixtures of solely halosilanes can  
10 be used, or a mixture of halosilane with alkoxy silane and/or acetoxy silane can be used.

[0021] The hydrolysable organosilane is preferably used at 0.1 to 10% or more by weight  
based on the stucco or other dry mineral or filler. Most preferably it is used at 0.5 to 5%  
based on the weight of stucco.  
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[0022] Generally, the hydrolysis of alkoxy groups of an organosilane such as an  
organotrialkoxysilane requires molecular contact of water with the alkoxy silane in the  
presence of a catalyst. Trialkoxysilanes hydrolyze stepwise in water to the corresponding  
silanols which condense to polysiloxanes. The hydrolysis of organotrialkoxysilanes is  
20 relatively rapid while the condensation reaction is slower.

[0023] If desired, the hydrolysable organosilane can be mixed with other silicon  
compounds, particularly a polyorganosiloxane such as a silanol-functional or alkoxy-  
functional polyorganosiloxane, for example a silanol-functional polydimethylsiloxane or  
25 alkoxy-functional polydimethylsiloxane. The silanol- functional polydimethylsiloxanes and  
alkoxy-functional polydimethylsiloxanes may contain terminal, pendant, or terminal and  
pendant, functional groups. Suitable functional polydimethylsiloxanes will generally have  
from 2-300 repeating units in the chain. These organosilicon compounds are capable of  
functioning as crosslinking agents and/or chain extenders in the polysiloxanes formed by  
30 condensation of the hydrolysable organosilane. If such another silicon compound is used,  
silanol- functional polydimethylsiloxanes having 4-100 repeating units in the chain are  
preferred. In general the hydrolysable organosilane is hydrolysed and then condensed to  
form a polysiloxane, although when a silanol-functional polysiloxane is present the  
hydrolysable groups of the silane can condense with the silanol groups to form an extended  
35 or crosslinked polysiloxane. The weight ratio of hydrolysable organosilane to silanol-

functional or alkoxy-functional polyorganosiloxane is preferably at least 1:10, more preferably at least 1:3, for example 1:1 to 10:1.

- [0024] The catalyst which is mixed with the gypsum and the hydrolysable organosilane can 5 be any catalyst known to be effective for hydrolysis and condensation of the organosilane. It can for example be a base catalyst, an organic compound of a metal such as a metal alkoxide, or a fluoride salt, or a combination of any of these, for example a base catalyst can be used in conjunction with a metal alkoxide.
- [0025] The base catalyst can in general be any strong or weak base. Some examples of 10 suitable bases include calcium oxide powder, calcium carbonate, solid calcium hydroxide or liquid lime, calcium acetate, sodium hydroxide, potassium hydroxide, sodium methylate, sodium carbonate, sodium bicarbonate, sodium borate, sodium acetate, solutions of a siliconate or silicate salt such as a sodium, potassium, calcium or aluminium siliconate or 15 silicate, fly ash, amines such as triethylamine, ethylenetriamine, butylamine, octylamine, dibutylamine, monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylenediamine, triethylenediamine, guanidine, diphenylguanidine, morpholine, laurylamine or N,N-dimethylbenzylamine, ammonium hydroxide, ammonium carbonate, ammonium 20 acetate, a phosphazene base, potassium acetate, magnesium carbonate, dolomite, potassium carbonate, sodium carbonate, magnesium oxide, cement such as Portland cement, sulphate resisting cement, blast furnace cement, pozzolanic cement, white cement, high alumina cement or expansive cement, and mixtures thereof. The pH generated in an aqueous slurry of stucco and organosilane with the base catalyst can be from 8-14. Strong 25 bases, capable of generating a pH of at least 10, preferably about 10-13, are effective catalysts in the process of the invention provided that the mineral or filler is not adversely affected by strong base. Sodium hydroxide is one example of a strong base. It can be added in solid form, e.g. flakes, or as an aqueous solution. Weaker bases, generating a pH of 8-10 in an aqueous slurry of stucco and organosilane, are also effective catalysts used 30 alone or in conjunction with an organic compound of a metal. The base catalyst is added to the stucco slurry in an amount sufficient to achieve the desired pH, typically in an amount of 0.1-1.0% based on the total weight of the stucco slurry.

- [0026] The organic compound of a metal can for example be a compound of titanium, tin, 35 aluminium, zirconium or vanadium. It can for example be a metal alkoxide or a metal

carboxylate salt or a chelated metal compound. Preferred titanium compounds are titanium alkoxides, otherwise known as titanate esters, for example a titanium tetraalkoxide such as titanium tetra-n-butoxide (tetrabutyl titanate), tetraethyl titanate, tetranonyl titanate or tetraisopropoxy titanate. A titanium chelate can be used, for example a chelated titanate 5 ester such as bis(acetylacetonyl) diisopropyl titanate or diisopropoxy titanium bis(ethylacetooacetate). The titanium tetraalkoxides are usually more catalytically active than the titanium chelate compounds. Analogous zirconium or vanadium compounds, for example zirconate or vanadate esters, can alternatively or additionally be used. Preferred aluminium compounds are aluminium alkoxides, for example aluminium sec-butanolate, or 10 aluminium chelate compounds.

[0027] If the organic compound of a metal is a tin compound it is usually a tin carboxylate or organotin carboxylate, for example dibutyltin dilaurate, dioctyltin dilaurate, stannous octoate, stannous acetate, stannous oxalate, stannous naphthenate, dibutyltin dioctoate, 15 dibutyltin bis(isooctyl maleate) or dioctyltin bis(isooctyl thioglycolate), although an organotin chelate compound such as dibutyltinbis(2,4-pentadionate)tin can be used. The combination of an organic compound of tin with an amine such as laurylamine can be particularly effective as a catalyst.

20 [0028] The amount of organic compound of a metal added as catalyst can for example be 0.01-2% based on the total weight of the stucco slurry, preferably 0.02-0.5%.

[0029] The fluoride salt added as hydrolysis and condensation catalyst in the method according to the invention is preferably an ammonium fluoride of the formula  $[R'', N]F$  in 25 which each R'' can be a hydrogen atom or a monovalent, optionally substituted hydrocarbon radical, for example methyl, ethyl, n-butyl, n-propyl, iso-propyl or benzyl, adducts thereof with carbonyl compounds such as a beta-ketocarboxylic acid esters or a 1,3-diketone, a metal fluoride such as potassium fluoride, cesium fluoride, zinc fluoride or copper fluoride, an organometallic fluoride such as dibutyltin fluoride, or an organic or inorganic ammonium 30 hydrogen fluoride, phosphonium fluoride, phosphonium hydrogen fluoride, tetrafluoroborate, hexafluorosilicate or fluorophosphate. Preferred ammonium fluorides include tetrabutylammonium fluoride, tetramethylammonium fluoride, benzylmethylammonium fluoride and methylammonium fluoride and adducts thereof with carbonyl compounds such as acetylacetone, methyl acetoacetate, 2-ethylhexyl acetoacetate, isopropyl acetoacetate or

ethyl acetoacetate. The amount of fluoride salt added as catalyst can for example be 0.01-5% based on the total weight of the stucco slurry, preferably 0.02-1%.

[0030] Combinations of two or more different catalysts can be used, for example different types of catalyst. A base catalyst can advantageously be used with an alkoxide of titanium, zirconium, vanadium or aluminium, an organic compound of tin or a fluoride salt.

[0031] The amount of water added is generally in excess of that required for the hydrolysis of the organosilane. The amount of water can for example be 100 parts of water per 0.1-50 parts by weight of organosilane, preferably 100 parts of water per 0.3-20 parts of organosilane. It may be arranged that sufficient water is mixed with the organosilane to form a slurry when subsequently mixed with stucco. Alternatively further water can be added with the catalyst or separately. Formation of a slurry of the stucco is convenient when preparing a gypsum product. The slurry can be discharged onto a support or mold, and dried to form a hydrophobic gypsum product. The ratio of water to stucco when forming a slurry is preferably 50-150 parts water per 100 parts by weight stucco, most preferably 60-100 parts water per 100 parts stucco.

[0032] When combined with the hydrolysable organosilane and water, the catalyst enhances formation of hydrolysed silanol and/or by condensation of silanols formed by hydrolysis of the organosilane to higher molecular weight siloxane species. Whilst it is preferred in the method of the invention to avoid such condensation to a polysiloxane network before the organosilane contacts the stucco, the catalyst may be introduced to the hydrolysable organosilane and water mix shortly, typically immediately before combination with the stucco to form a slurry. We have found that if the organosilane is hydrolysed in the presence of the gypsum or other mineral or filler, so that the organosilane hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler, the polyorganosiloxane becomes intimately incorporated in the mineral or filler. In the case of stucco, the hydrolysable silane is contacted with  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  and water so that the silane goes through hydrolysis-condensation into a higher molecular weight siloxane or resin while the calcium sulfate hemihydrate is crystallizing or setting into dehydrate or gypsum. The mixing and setting takes place within minutes and the silane is rapidly hydrolysed and condensed while the gypsum is crystallizing improved compatibility, affinity or anchorage of the siloxanes to the gypsum is achieved, imparting durable hydrophobicity.

[0033] Thus one preferred procedure according to the invention for preparing hydrophobic gypsum comprises mixing stucco with a hydrolysable organosilane and contacting the resulting mixture with a catalyst for hydrolysis and condensation of the organosilane, water being present when the said mixture is contacted with the catalyst. The water can be added 5 with the organosilane by feeding the organosilane as an aqueous composition, or a liquid organosilane can be mixed with stucco followed by mixing with aqueous catalyst, or both the organosilane and the catalyst can be added as aqueous compositions. Alternatively both the organosilane and the catalyst can be added in non-aqueous form, and water can be admixed subsequently.

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[0034] An alternative preferred procedure according to the invention for preparing hydrophobic gypsum comprises mixing stucco with a hydrolysable organosilane and simultaneously with a catalyst for hydrolysis and condensation of the organosilane, water being present as the stucco, organosilane and catalyst are mixed. Either or both of the 15 organosilane and the catalyst can be admixed with the stucco as an aqueous composition. The stucco can be admixed as an aqueous slurry, in which case the organosilane and the catalyst can each be admixed as an aqueous composition or in non-aqueous form.

[0035] In a further alternative preferred procedure according to the invention the stucco 20 can be mixed with the catalyst and then contacted with the hydrolysable organosilane. For example the stucco can be mixed with an aqueous solution of catalyst to form a gypsum slurry and then contacted with the organosilane. Alternatively the stucco can be mixed as a powder with a solid catalyst and then contacted with aqueous organosilane. Examples of 25 solid base catalysts which can advantageously be mixed in this manner are sodium hydroxide flakes, calcium oxide powder, solid calcium hydroxide, calcium carbonate, dolomite, fly ash, cement.

[0036] If the organosilane is added as an aqueous composition in any of the above 30 procedures, it is preferred that the aqueous composition is not prepared a long time before contacting the stucco or other mineral or filler, to minimize any hydrolysis and/or condensation of the organosilane which may take place even in the absence of catalyst.

[0037] As noted above, other additives for making gypsum plasterboard are often used in 35 commercial operations including starch; foaming agents; wetting agents; accelerators; retarders such as proteins and organic acids; paper or pulp; viscosity modifying agents; anti-

burning agents; non-silicon atom containing water-resisting chemicals such as wax emulsions; glass fibers; fire-resistance enhancers such as vermiculite, clays, and fumed silica; and polymeric compounds such as polyvinyl alcohol. One or more additives such as these may be included in the present process. They can for example be mixed with the stucco before it contacts the organosilane and catalyst.

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[0038] In addition to hydrophobing gypsum and gypsum products, the polysiloxane formed from the hydrolysable organosilane imparts other advantages known to be given by polysiloxanes and may do so more effectively because of its more even distribution in the 10 gypsum product. It functions as a foaming aid, a dispersing aid, a density reducer, a viscosity modifier, or a dimension stabilizer of the gypsum product, and may increase mechanical strength, durability, and stiffness, reduce brittleness and burning, enhance fire resistance and mould resistance, and promote bonding and adhesion, for example coupling with vermiculite, clay, silica, starch, pulp, paper, glass, or glass fibers.

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[0039] The following examples are set forth in order to illustrate the invention in more detail. Parts and percentages are by weight unless otherwise stated.

#### EXAMPLE 1

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[0040] To 80 g of tap water was added 0.5 g of methyltrimethoxysilane (MTM) under a vigorous stirring for few minutes. 100 g of natural stucco and several drops of a 40 weight percent aqueous solution of NaOH to adjust the pH to around 12 were then added under vigorous stirring. The slurry was stirred for another 60 seconds and poured into disk shaped molds. The samples were allowed to set at room temperature (20-25 °C) for 15-60 minutes. 25 The disks separated from the molds were gypsum disks of three centimeter in diameter and one centimeter in depth. The samples were further dried in an air circulating oven for 30 minutes at 110 °C, and then for 12-24 hours at 40 °C. The disks were cooled down and immersed in water for two hours. The weight of the disks before and after immersing the 30 disks in water was measured. The water uptake expressed in percent, was used as the measure of the hydrophobing property of the silane composition.

EXAMPLES 2-22

[0041] Example 1 was repeated using varying amounts of MTM, vinyltrimethoxysilane (VTM), methyltriethoxysilane (MTE), methyltripropoxysilane (MTP), methyltriacetoxysilane (MTA), a MTA/ethyltriacteoxysilane blend (M/ETA), vinyltriethoxysilane (VTE) or vinyl triacetoxysilane (VTA). The water uptake of the disks treated with each organosilane was compared to the water uptake of untreated gypsum that has a value of about 45 percent. Table 1 shows results obtained by following the above procedure.

TABLE 1 - WATER UPTAKE

Example No.	Silane	Weight Percent of silane vs. calcium sulfate hemihydrate	Catalyst	Water Uptake, Percent
Control	None	—	None	45.0
Control	None	—		46.4
1	MTM	0.5		34.1
2		0.75		16.3
3		1		7.5
4		2		2.7
5		3		1.3
6		5		0.8
7		0.5		43.4
8	VTM	1		22.4
9		5		1.1
10		0.5		43.9
11	MTE	0.75		41.4
12		1		30.9
13		2		1.1
14		3		1.6
15		5		2.4
16	MTP	5		2.6
17	MTA	0.5		5.8
18	VTE	0.5		15.2
19		0.5		45.2
20		1		25.6
21		5		1.9
22	VTA	0.5	NaOH	7.4

[0042] Examples 1-18 and Table 1 show that a reduction in water-absorption, and the  
 5 consequent improvement in water resistance, was obtained at various loadings of the silane.  
 In particular, markedly lower water uptake percentages were obtained using MTM at only 1  
 to 2% based on stucco and MTA at only 0.5% based on stucco.

EXAMPLE 23

[0043] To 80 g of tap water was added 0.5 g of methyltrimethoxysilane and 0.5 g of a hydroxy-terminated polydimethylsiloxane (PDMS) sold by Dow Corning under the trademark DC 4-7041 under a vigorous stirring for few minutes. DC 4-7041 designates a hydroxy-terminated PDMS of average degree of polymerisation (DP) of around 4. 100 g of natural stucco and several drops of a 40 weight percent aqueous solution of NaOH to adjust the pH to around 12 were then added under vigorous stirring. The slurry was stirred for another 60 seconds and poured into disk shaped molds. The samples were then treated and tested as described in Example 1.

EXAMPLES 24-33

[0044] Example 28 was repeated using various amounts of MTM mixed in different ratios with DC4-7041 or two other hydroxy-terminated polydimethylsiloxanes. DC 4-2737 and DC 1-3563 designate Dow Coming hydroxy-terminated PDMS of average DP 12 and 40 respectively. Table 2 shows the results obtained for water uptake.

TABLE 2 - WATER UPTAKE

Example No.	Silane	HO-terminated siloxane	HO-terminated siloxane:silane ratio	Weight Percent of silane/HO-terminated siloxane vs. calcium sulfate hemihydrate	Catalyst	Water Uptake, Percent	
Control	None	None	—	—	None	45.0	
Control	None	None	—	—	NaOH	46.4	
Control	DC 4-7041	DC 4-7041	100:0	1		44.8	
23			50:50			39.3	
24			25:75			6.5	
Control			100:0			42.3	
25		DC 4-2737	75:25	5		41.2	
26			50:50			40.8	
27			25:75			2.2	
Control			100:0			37.3	
28	MTM	DC 4-2737	75:25	5		40.7	
29			50:50			16.4	
30			25:75			2.1	
Control		DC 1-3563	100:0			37.8	
31			75:25	5		1.7	
32			50:50			1.8	
33			25:75			1.7	

[0045] Examples 23-33 and Table 2 show that a reduction in water-absorption, and the  
 5 consequent improvement in water resistance, was obtained by blending hydroxy-terminated  
 PDMS with silane at various ratios compared to the use of pure hydroxy-terminated PDMS.

#### EXAMPLE 34

10 [0046] In this example, the silane was mixed without the use of catalyst. To 80 g of tap  
 water was added under a vigorous stirring 2.0 g of a 25:75 by weight mixture of  
 methyltriacetoxysilane and methyltrimethoxysilane and 100 g of natural stucco. No further  
 catalyst was added, and the pH of the resulting slurry was measured to be about 6-7. The

slurry was stirred for another 60 seconds and poured into disk shaped molds. The samples were then treated and tested as described in Example 1.

#### EXAMPLES 35-37

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[0047] In Examples 35 to 37, Example 34 was repeated using varying amounts of MTA, MTM and/or MTP. Table 3 shows results on water uptake obtained.

TABLE 3 - WATER UPTAKE

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Example No.	Silane	Weight Percent of silane vs. calcium sulfate hemihydrate	Catalyst	Water Uptake, Percent
Control	None	—	None	45.0
33	MTA:MTM 25:75	2	None	3.2
34	MTA:MTM 50:50	2	None	2.8
35	MTA:MTP 50:50	2	None	7.3
36	MTA:MTP 75:25	1	None	11.7

[0048] Examples 33-36 and Table 2 show that a reduction in water-absorption, and hence increased water resistance, was observed when the organosilane was hydrolysed in the presence of the stucco even without use of catalyst.

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CLAIMS

1. A method of preparing a hydrophobic mineral and/or filler comprising contacting the mineral and/or filler in powder form with a hydrolyzable organosilane, water and a catalyst for hydrolysis and condensation of the organosilane under conditions such that the organosilane is hydrolysed in the presence of the mineral and/or filler and the organosilane hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler.
2. A method according to Claim 1, in which the minerals and/or fillers comprise non-hydrated, partially hydrated, or hydrated, fluorides, chlorides, bromides, iodides, chromates, carbonate hydroxides, hydroxides, phosphates, hydrogen phosphates, nitrates, oxides, sulphates of sodium, potassium, magnesium, calcium, and barium, titanium dioxide, zinc oxide, aluminium oxide, aluminium trihydroxide, vermiculite, silica, fumed silica, fused silica, precipitated silica, quartz, sand, silica gel, rice hull ash, ceramic and glass beads, zeolites, hydrous calcium silicate, silica-carbon black composite, functionalized carbon nanotubes, cement, fly ash, slate flour, bentonite, clay, mica, kaolin, talc, calcium carbonate, wollastonite, polymeric fillers, rubber particles, wood flour, wood fibers, cellulose and cellulose-containing products, aramid fibers, nylon fibres, cotton fibers, or glass fibers.
3. A method according to claim 1 for preparing hydrophobic gypsum in which the mineral and/or filler in powder form is stucco and optionally gypsum.
4. A method according to Claim 3 comprising mixing stucco with a hydrolysable organosilane and contacting the resulting mixture with the catalyst, water being present when the said mixture is contacted with the catalyst.
5. A method according to Claim 3 comprising mixing stucco with a hydrolysable organosilane and simultaneously with the catalyst for hydrolysis and condensation of the organosilane, water being present as the stucco, organosilane and catalyst are mixed.
6. A method according to any of Claims 1 to 5, characterized in that the hydrolysable organosilane comprises one or more silanes, each silane being the same or

different and comprising one or more alkoxy groups and/or one or more acetoxy groups and/or one or more chloride groups and mixtures thereof.

7. A method according to Claim 6, characterized in that the hydrolysable organosilane has the formula  $\text{RSi(OR')}_3$ , wherein R represents an alkyl or alkenyl group having 1 to 18 carbon atoms and R' represents an alkyl group having 1 to 4 carbon atoms
8. A method according to Claim 7, characterized in that the hydrolysable organosilane comprises methyltrimethoxysilane.
9. A method according to Claim 7, characterized in that the hydrolysable organosilane comprises vinyltrimethoxysilane.
10. A method according to claim 6 characterized in that the hydrolysable organosilane comprises a mixture containing at least two of methyltripropoxysilane and/or methyltrimethoxysilane and/or methyltriacetoxysilane and/or alkenyltrialkoxysilane and/or alkenyltriacetoxysilane
11. A method according to Claim 6, characterized in that the hydrolysable organosilane is methyltriacetoxysilane or vinyltriacetoxysilane.
12. A method according to any of Claims 1 to 11, characterized in that the hydrolysable organosilane is mixed with a polyorganosiloxane.
13. A method according to Claim 12, characterized in that the polyorganosiloxane is a silanol- functional polydimethylsiloxane.
14. A method according to any of Claims 1 to 13, characterized in that the catalyst is a base.
15. A method according to any of Claims 1 to 13, characterized in that the catalyst is an alkoxide of titanium, zirconium, vanadium or aluminium.
16. A method according to any of Claims 1 to 13, characterized in that the catalyst is an organic compound of tin.

17. A method according to any of Claims 1 to 13, characterized in that the catalyst is a fluoride salt.
18. A method according to Claim 14, characterized in that the catalyst comprises a base and an alkoxide of titanium, zirconium, vanadium or aluminium, an organic compound of tin or a fluoride salt.
19. A method of preparing a hydrophobic mineral and/or filler comprising contacting the mineral and/or filler in powder form with a hydrolyzable organosilane and water, the hydrolysable silane being a mixture of an alkyltriacetoxysilane and an alkyltrialkoxysilane, under conditions such that the organosilane is hydrolysed in the presence of the mineral and/or filler and the organosilane hydrolysis product condenses to form polyorganosiloxane in the presence of the mineral or filler.
20. A method according to any of Claims 3 to 19, characterized in that the hydrolysable organosilane is present at 0.1 to 10% based on the weight of stucco.
21. A method according to any of Claims 3 to 20, characterized in that the amount of water present is sufficient to form a slurry.
22. A method according to Claim 21 for preparing a gypsum product, characterized by discharging the slurry onto a support or mold, and drying the slurry to form a hydrophobic gypsum or hydrophobic gypsum product.
23. Hydrophobic gypsum or gypsum product prepared by the process of any of Claims 3 to 22.
24. Hydrophobic gypsum, characterized in that the gypsum incorporates organopolysiloxane formed by condensation of an organosilane in the presence of the gypsum, the hydrophobic gypsum having a water uptake of below 25% by weight.



Patent Office

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**Application No:** GB0623265.6  
**Claims searched:** 1-18 and 20-22 in part

**Examiner:** Hayley Yates  
**Date of search:** 7 March 2007

### Patents Act 1977: Search Report under Section 17

#### Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1, 2, 6, 7, 14 and 16	EP 0047746 A Pühringer; see page 5 lines 4-11 and page 10 line 9 to page 11 line 31
A	-	GB994009 A Dow Corning Corporation; see whole document
A	-	US 2006/0107876 A Sandmeyer et al; srr abstract
A	-	WO 02/30847 A Windridge et al; see abstract
A	-	US 4136687 A Dabroski; see column 2 line 18 to column 3 line 59
A	-	CN 1105345 A Zhang; see abstract translation

#### Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

#### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>X</sup>:

[redacted]  
Worldwide search of patent documents classified in the following areas of the IPC

C04B

The following online and other databases have been used in the preparation of this search report

[redacted]  
WPI & EPQDOC